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54 Radiation curable composition with high temperature oil resistance.

57 The present invention relates to a radiation curable composition with high temperature oil resistance comprising

- (1) a (meth)acrylated urethane component comprising
 - (a) the reaction product of hydroxyethyl(meth)acrylate and a monomeric or polymeric aromatic isocyanate,
 - (b) hydroxyethyl(meth)acrylate and optionally
 - (c) a (meth)acrylated prepolymer of a monomeric or polymeric aromatic isocyanate and at least one polycaprolactone polyol with a functionality ≥ 2 and a molecular weight in the range of about 500 to about 3000, or
 - (d) a (meth)acrylated prepolymer of a monomeric or polymeric aromatic isocyanate and at least one polyether polyol with a functionality ≥ 2 and a molecular weight in the range of about 90 to about 7000, or a mixture of (c) and (d),
 - (2) an aromatic multifunctional epoxy (meth)acrylate having a molecular weight of less than about 1000,
 - (3) at least one free radical polymerizable monomer and
 - (4) a free radical photoinitiator,
- which composition exhibits at 25°C (i) a T_g greater than about 45°C, (ii) an elongation of greater than about 3%, (iii) a tensile strength of greater than about 9 N/mm² and (iv) a shear storage modulus of greater than about 30 N/mm².

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The present invention is directed to a radiation curable composition with high temperature oil resistance useful in adhesive applications requiring a combination of chemical, temperature and fatigue resistance, in particular in the construction of oil and chemical filters.

Prior art adhesives useful in the construction of oil and chemical filters are PVC plastisol in nature and require a heat cure. The radiation curable composition of the present invention offers significant productivity improvements over the prior art heat cured adhesives in terms of lowering of cure time.

As compared with existing UV curable adhesives, the radiation curable composition of the present invention offers a unique combination of temperature resistance, chemical resistance and toughness.

Accordingly, it is a primary object of the present invention to provide a radiation curable composition which exhibits at 25°C (i) a T_g greater than about 45°C, (ii) an elongation of greater than about 3%, (iii) a tensile strength of greater than about 9 N/mm² (1300 psi) and (iv) a shear storage modulus of greater than about 30 N/mm² (4300 psi).

Further objects and advantages of this invention will become apparent from the following descriptive material and illustrative examples.

The present invention provides a radiation curable composition with high temperature oil resistance useful in adhesive applications requiring a combination of chemical, temperature and fatigue resistance.

The present invention relates to a radiation curable composition with high temperature oil resistance comprising

(1) a (meth)acrylated urethane component comprising

(a) the reaction product of hydroxyethyl(meth)acrylate and a monomeric or polymeric aromatic isocyanate,

(b) hydroxyethyl(meth)acrylate, and optionally

(c) a (meth)acrylated prepolymer of a monomeric or polymeric aromatic isocyanate and at least one polycaprolactone polyol with a functionality ≥ 2 and a molecular weight in the range of about 500 to about 3000 or

(d) a (meth)acrylated prepolymer of a monomeric or polymeric aromatic isocyanate and at least one polyether polyol with a functionality ≥ 2 and a molecular weight in the range of about 90 to about 7000, or a mixture of (c) and (d),

(2) an aromatic multifunctional epoxy (meth)acrylate having a molecular weight of less than about 1000,

(3) at least one free radical polymerizable monomer and

(4) a free radical photoinitiator,

which composition exhibits at 25°C (i) a T_g greater than about 45°C, (ii) an elongation of greater than about 3%, (iii) a tensile strength of greater than about 9 N/mm² (1300 psi) and (iv) a shear storage modulus of greater than about 30 N/mm² (4300 psi).

The (meth)acrylated urethane component provides the composition with excellent toughness and low shrinkage. The (meth)acrylated urethane component is prepared by reacting the monomeric or polymeric aromatic isocyanate with an excess of hydroxyethyl(meth)acrylate, preferably hydroxyethylmethacrylate (HEMA), thereby producing components (a) and (b).

Component (a) is present in an amount ranging from about 50 to about 99% by weight, preferably about 80 to about 99% by weight, and most preferably about 94% by weight, based upon the total weight of component (1).

Component (b) is present in an amount ranging from about 1 to about 50% by weight, preferably about 1 to about 20% by weight, and most preferably about 6% by weight, based upon the total weight of component (1).

Suitable aromatic isocyanates include methylene bis-(4-isocyanato benzene), toluene diisocyanate, 3,3'-toluidine-4,4'-diisocyanate, 3,3'-dimethyl-diphenylmethane-4,4'-diisocyanate, 1,5-diisocyanato-naphthalene, 1,4-diisocyanato-benzene and 1,4- and 1,3-di-(isocyanato-dimethyl)-benzene. Preferably, methylene bis-(4-isocyanato benzene) is used. Monomeric aromatic isocyanates are preferred although the polymeric aromatic isocyanates are also suitable. The polymeric aromatic isocyanates preferably have a molecular weight of about 250 to about 500, most preferably, about 250 and have a functionality of about 2 to about 3, preferably about 2.0.

The (meth)acrylated urethane component can, in addition to components (a) and (b), further comprise component (c), (d) or a mixture thereof. The mixture can be prepared by reacting the aromatic isocyanate and the polycaprolactone polyol and/or the polyether polyol to form a prepolymer. The prepolymer is then reacted with the hydroxyethyl(meth)acrylate, preferably HEMA.

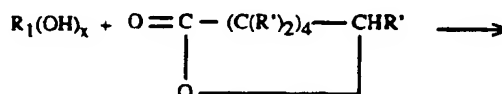
The reaction of the polyol with the aromatic isocyanate is carried out under nitrogen and at a temperature of from about 40°C to about 100°C, preferably from about 60°C to about 90°C and most preferably from about 80°C to about 85°C, for about 2 to about 24 hours depending upon the reaction temperature. Hydroxyethyl-

(m th)acrylate is then added to the reaction mixture, preferably with an inhibitor, at the same temperature and the reaction is continued for about 3 to about 5 hours. Suitable inhibitors include butylated hydroxy toluene, hydroquinone, phenothiazine, monomethylether of hydroquinone, naphthaquinone, benzoquinone and the like.

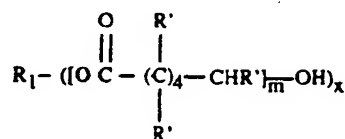
Suitable polycaprolactone polyols that can be used to prepare component (c) include any of the known polycaprolactone polyols that are commercially available and that are fully described, for example, in U.S. Patent No. 3,169,945. As described in this patent the polycaprolactone polyols are produced by the ring-opening polymerization of an excess of a caprolactone and an organic polyfunctional initiator having at least two reactive hydrogen atoms. The organic functional initiators can be any polyhydroxyl compound as is shown in U.S. Patent No. 3,169,945. Illustrative thereof are the diols such as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, dipropylene glycol, 1,3-propylene glycol, polyethylene glycol, polypropylene glycol, poly(oxyethylene-oxypropylene) glycols, neopentyl glycol, 1,4-cyclohexanedimethanol, 2,4,4-trimethyl-pentandiol, 2,2-dimethyl-3-hydroxy-propyl, 2,2-dimethyl-3-hydroxypropionate, and similar polyalkylene glycols, either blocked, capped or heteric, containing up to about 40 or more alkyleneoxy units in the molecule, 3-methyl-1,5-pentandiol, cyclohexanediol, 4,4'-methylene-bis-cyclohexanol, 4,4'-isopropylidene-bis-cyclohexanol, xylenediol, 2-(4-hydroxymethylphenyl) ethanol, 1,4-butanediol, 1,6-hexanediol and the like; triols such as glycerol, trimethylolpropane, 1,2,6-hexanetriol, triethanolamine, triisopropanolamine, and the like; tetrols such as erythritol, pentaerythritol, N,N,N',N'-tetrakis-(2-hydroxyethyl)-ethylene diamine, and the like.

When the organic functional initiator is reacted with the caprolactone a reaction occurs that can be represented in its simplest form by the equation:

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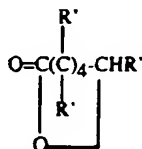
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In this equation the organic functional initiator is the $R_1(OH)_x$ compound and the caprolactone is the

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compound. This can be ϵ -caprolactone itself or a substituted caprolactone wherein R' is an alkyl, alkoxy, aryl, cycloalkyl, alkaryl or aralkyl group having up to twelve carbon atoms and wherein at least six of the R' groups are hydrogen atoms, as shown in U.S. Patent No. 3,169,945. The polycaprolactone polyols that are used are shown by the formula on the right hand side of the equation. They can have an average molecular weight of from about 500 to about 3,000. The preferred polycaprolactone polyol compounds are those having an average molecular weight of from about 500 to about 3000, most preferably from about 800 to about 2000. The most preferred are the polycaprolactone diol compounds having an average molecular weight of from about 800 to about 1200 and the polycaprolactone triol and tetrol compounds having an average molecular weight of from about 800 to about 1000. In the formula, m is an integer representing the average number of repeating units needed to produce the compound having said molecular weights. The hydroxyl number of the polycaprolactone polyol can be from about 30 to about 600, preferably from about 100 to about 200, and the polycaprolactone can have an average of from about 2 to about 8, preferably 2 to 4, hydroxyl groups.

Illustrative of polycaprolactone polyols that can be used in the compositions of this invention, one can mention the reaction products of a polyhydroxyl compound having an average of from 2 to 6 hydroxyl groups with caprolactone. The manner in which these type polycaprolactone polyols is produced is shown in U.S. Patent No. 3,169,945 and many such compositions are commercially available. In the following table there are listed illustrative polycaprolactone polyols. The first column lists the organic functional initiator that is reacted with

the caprolactone polyol shown in the second column. Knowing the molecular weights of the initiator and of the polycaprolactone polyol one can readily determine the average number of molecules of caprolactone (CPL Units) that reacted to produce the compounds. This figure is shown in the third column.

5	<u>Polycaprolactone polyols</u>		
10	Initiator	Average M _w of polyol	Average No. of CPL units in molecules
15	Ethylene glycol	290	2
	Ethylene glycol	803	6.5
	Ethylene glycol	2114	18
	Propylene glycol	874	7
20	Octylene glycol	602	4
	Decalene glycol	801	5.5
	Diethylene glycol	527	3.7
	Diethylene glycol	847	6.5
25	Diethylene glycol	1246	10
	Diethylene glycol	1998	16.6
	Diethylene glycol	3526	30
	Triethylene glycol	754	5.3
30	Polyethylene glycol (MW 200)*	713	4.5
	Polyethylene glycol (MW 600)*	1398	7
	Polyethylene glycol (MW 1500)*	2868	12
	1,2-Propylene glycol	646	5
35	1,3-Propylene glycol	988	8
	Dipropylene glycol	476	3
	Polypropylene glycol (MW 425)*	835	3.6
	Polypropylene glycol (MW 1000)*	1684	6

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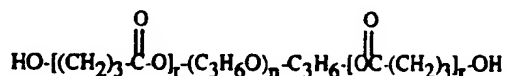
	Polypropylene glycol (MW 2000)*	2456	4
	Hexylene glycol	916	7
5	2-Ethyl-1,3-hexanediol	602	4
	1,5-Pentanediol	446	3
	1,4-Cyclohexanediol	629	4.5
	1,3-Bis(hydroxyethyl)-benzene	736	5
10	Glycerol	548	4
	1,2,6-Hexanetriol	476	3
	Trimethylolpropane	590	4
15	Trimethylolpropane	750	5.4
	Trimethylolpropane	1103	8.5
	Triethanolamine	890	6.5
	Erythritol	920	7
20	Pentaerythritol	1219	9.5
	1,4-Butanediol	546	4.0
	Neopentyl glycol	674	5.0

* Average molecular weight of glycol

The structures of the compounds in the above tabulation are obvious to one skilled in the art based on the information given. The structure of 7th compound in the table above is idealized as



wherein the variable r is an integer, the sum of r+r has an average value of 3.7 and the average molecular weight is 527. The structure of 20th compound in the table above is idealized as



wherein the sum of r+r has an average value of 6 and the average molecular weight is 1684. This explanation makes explicit the structural formulas of the compounds set forth above.

Polycaprolactone hexols suitable for use in the present invention can be prepared by the catalytic polymerization of an excess of polycaprolactone polyols and a cycloaliphatic epoxide. Illustrative polycaprolactone polyols useful in the preparation of polycaprolactone hexols include polycaprolactone diols, polycaprolactone triols and the like, including mixtures thereof. Many of these polycaprolactone polyols are commercially available from Union Carbide Corporation. Cycloaliphatic epoxides suitable for use in preparing the polycaprolactone hexols include 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, bis-(3,4-epoxycyclohexylmethyl) adipate, vinyl cyclohexene dioxide and the like. Many of these cycloaliphatic epoxides are commercially available from Union Carbide Corporation. A suitable polymerization catalyst is diethylammonium triflate which is commercially available from the 3M Company as FC-520.

A preferred method for preparation of the polycaprolactone hexols comprises adding one or more polycaprolactone triols to a reactor, heating the polycaprolactone triols to a temperature of about 100°C and adding the catalyst using a nitrogen sparge as soon as the polycaprolactone triols are molten. The polycaprolactone triols and catalyst mixture is then heated to a temperature of from about 150°C to about 200°C and a cycloaliphatic epoxide is added to the mixture. The reaction is carried out for about one hour to about three hours or

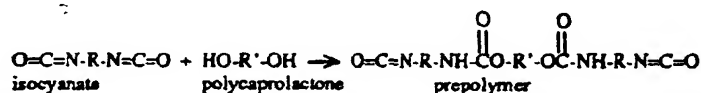
until the oxirane content has been reduced to a nil or almost a nil value. A modification of this process can involve initially adding all of the ingredients into the reactor. A further modification of this method can involve a vacuum treatment of from 10 to 30 minutes after the catalyst addition and/or the use of a vacuum during the heating of the polycaprolactone triols to a molten state. Preferred polycaprolactone hexols have an average molecular weight of from about 500 to about 3000.

TONE® 0310 from Union Carbide Corporation is the preferred polycaprolactone polyol. Component (c) preferably is the reaction product of methylene bis-(4-isocyanatobenzene) and a polycaprolactone triol.

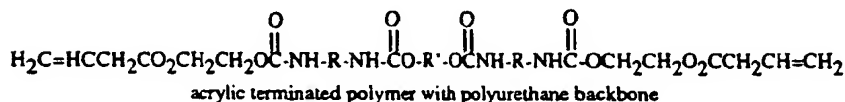
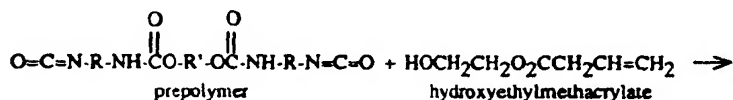
The polycaprolactone polyol is reacted with the aromatic isocyanate, preferably, methylene bis-(4-isocyanatobenzene), in a molar ratio of about 0.2:1 to about 0.6:1 preferably about 0.3:1 to about 0.5:1, and most preferably about 0.4:1 to produce the prepolymer of component (c).

Preparation of a mixture of (a), (b) and (c) is exemplified in reaction scheme 1 (an excess of HEMA is used thereby producing (b) which is not shown):

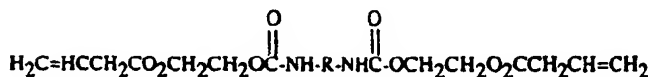
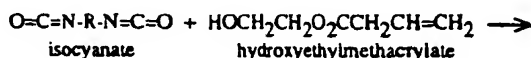
Reaction Scheme 1:



Primary:



Competing:



When component (1) contains component (a), (b) and (c), component (a) is present in an amount ranging from about 5 to about 35% by weight, preferably about 10 to about 30% by weight, and most preferably about 23% by weight, based upon the total weight of component (1). Component (b) is present in an amount ranging from about 1 to about 20% by weight, preferably about 1 to about 10% by weight, and most preferably about 6% by weight, based upon the total weight of component (1). Component (c) is present in an amount ranging from about 50 to about 90% by weight, preferably about 70 to about 80% by weight, and most preferably about 71% by weight, based upon the total weight of component (1).

Component (1) may further include, in addition to or in lieu of component (c), a (meth)acrylated prepolymer of a monomeric or polymeric aromatic isocyanate and at least one polyether polyol with a functionality of ≥ 2 and a molecular weight in the range of about 90 to about 7000 (i.e. component (d)).

Suitable polyether polyols include alkylene oxide adducts of polyhydroxyalkanes, alkylene oxide adducts of non-reducing sugars and sugar derivatives and the polyols from natural oils such as castor oil and the like.

Illustrative alkylene oxide adducts of polyhydroxyalkanes include, among others, the alkylene oxide ad-

ducts of ethylene glycol, propylene glycol, 1,3-dihydroxypropane, 1,3-dihydroxybutane, 1,4-dihydroxybutane, 1,4-, 1,5-, and 1,6-dihydroxyhexane, 1,2-, 1,3-, 1,4-, 1,6-, and 1,8-dihydroxyoctane, 1,10-dihydroxydecane, glycerol, 1,2,4-trihydroxybutane, 1,2,6-trihydroxyhexane, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, pentaerythritol, polycaprolactone, xylitol, arabitol, sorbitol, mannitol, and the like. A preferred class of alkylene oxide adducts of polyhydroxyalkanes are the ethylene oxide, propylene oxide, butylene oxide, or mixtures thereof, adducts of trihydroxyalkanes.

A further class of polyether polyols which can be employed are the alkylene oxide adducts of the non-reducing sugars, wherein the alkylene oxides have from 2 to 4 carbon atoms. Among the non-reducing sugars and sugar derivatives contemplated are sucrose, alkyl glycosides such as methyl glucoside, ethyl glucoside, and the like, glycol glycosides such as ethylene glycol glucoside, propylene glycol glucoside, glycerol glucoside, 1,2,6-hexanetriol glycoside, and the like, as well as the alkylene oxide adducts of the alkyl glycosides as set forth in U.S. Patent No. 3,073,788.

The polyols described hereinabove can have hydroxyl numbers which vary over a wide range. In general, the hydroxyl numbers of the above described polyols employed in this invention can range from about 15, and lower, to about 900, and higher. The hydroxyl number is defined as the number of milligrams of potassium hydroxide required for the complete neutralization of the fully phthalated derivative prepared from 1 gram of polyol. The hydroxyl number can also be defined by the equation:

$$\text{OH} = [(56.1 \times 1000 \times f) / \text{m.w.}]$$

where

OH = hydroxyl number of the polyol,

f = functionality, that is, average number of hydroxyl groups per molecule of polyol and

m.w. = molecular weight of the polyol.

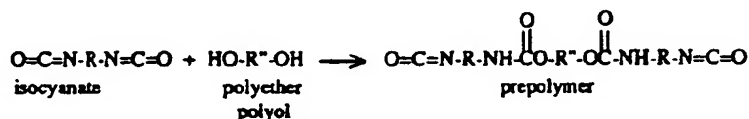
Further polyether polyols which are suitable for the preparation of component (d) include poly(oxypropylene)-poly(oxyethylene) block copolymers and nitrogen containing polyether polyols such as poly(oxyethylene)-poly(oxypropylene) block copolymers with ethylenediamine.

The polyether polyols described hereinabove can be prepared by conventional methods and are commercially available from a number of manufacturers. The preferred polyether polyols are poly(oxypropylene)-poly(oxyethylene) block copolymers.

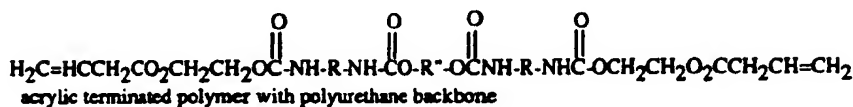
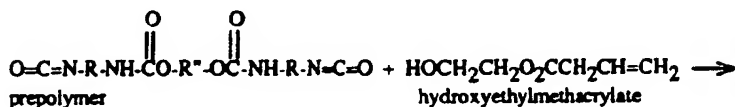
The polyether polyol is reacted with the aromatic isocyanate, preferably, methylene-bis-4 (-isocyanatobenzene), in a molar ratio of about 0.1:1 to about 0.8:1, preferably about 0.1:1 to about 0.3:1 mole, and most preferably about 0.2:1 to produce the prepolymer of component (d).

Preparation of a mixture of (a), (b) and (d) is exemplified in reaction scheme 2 and preparation of a mixture of (a), (b), (c) and (d) is exemplified in reaction scheme 3 as follows (an excess of HEMA is used thereby producing (b) which is not shown):

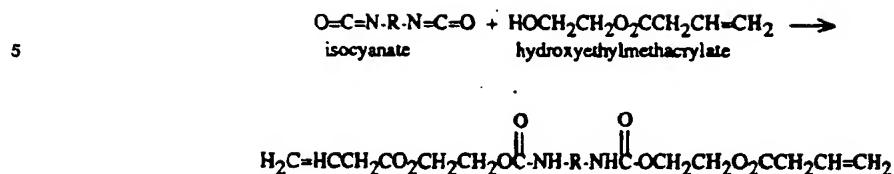
Reaction Scheme 2:



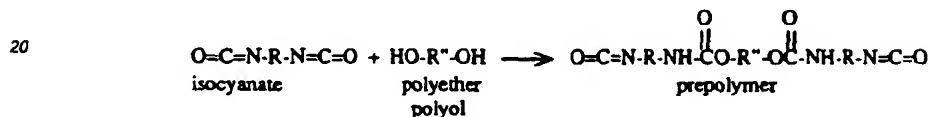
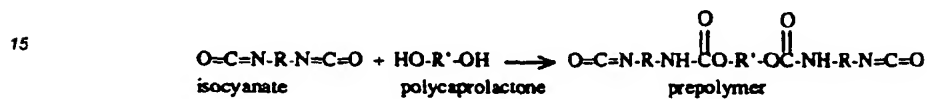
Primary:



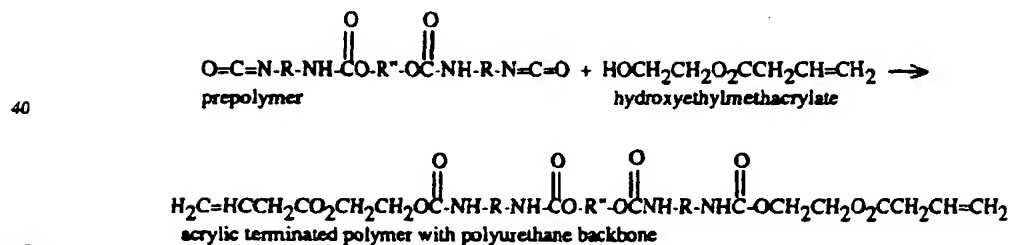
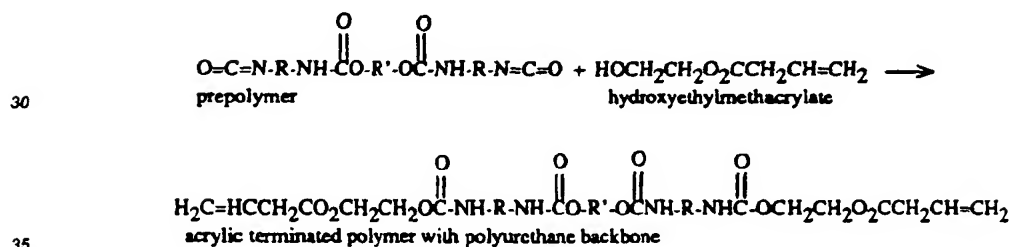
Competing:



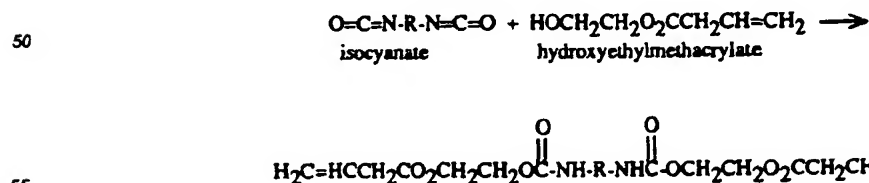
Reaction scheme 3:



Primary:



Competing:



When component (1) contains components (a), (b) and (d), component (a) is present in an amount ranging from about 10 to about 30% by weight, preferably about 20 to about 30% by weight, and most preferably about

23% by weight, based upon the total weight of component (1). Component (b) is present in an amount ranging from about 1 to about 20% by weight, preferably about 5 to about 15% by weight, and most preferably about 6% by weight, based upon the total weight of component (1). Component (d) is present in an amount ranging from about 50 to about 90% by weight, preferably about 60 to about 90% by weight, and most preferably about 71 % by weight, based upon the total weight of component (1).

When component (1) contains components (a), (b), (c) and (d), component (a) is present in an amount ranging from about 10 to about 50% by weight, preferably about 20 to about 30% by weight, and most preferably about 23 % by weight, based upon the total weight of component (1). Component (b) is present in an amount ranging from about 1 to about 20% by weight, preferably about 5 to about 15% by weight, and most preferably about 6% by weight, based upon the total weight of component (1). Component (c) is present in an amount ranging from about 1 to about 10% by weight, preferably about 1 to about 5% by weight, and most preferably about 3% by weight, based upon the total weight of component (1). Component (d) is present in an amount ranging from about 25 to about 75% by weight, preferably about 50 to about 75% by weight, and most preferably about 68% by weight, based upon the total weight of component (1).

Component (1) preferably includes components (a), (b), (c) and (d). In a particularly preferred embodiment, component (1) comprises

- (a) the reaction product of hydroxyethylmethacrylate and methylene bis-(4-isocyanato benzene),
- (b) hydroxyethylmethacrylate,
- (c) a methacrylated prepolymer of methylene bis-(4-isocyanato benzene) and at least one polycaprolactone polyol with a functionality ≥ 2 and a molecular weight in the range of about 500 to about 3000, and
- (d) a methacrylated prepolymer of methylene bis(4-isocyanato benzene) and at least one polyether polyol with a functionality ≥ 2 and a molecular weight in the range of about 90 to about 7,000.

Suitable aromatic multifunctional epoxy (meth)acrylates include virtually all aromatic epoxy resins containing on average at least two 1,2-epoxy groups per molecule which can be (meth)acrylated by methods well known in the art.

Illustrative examples of such aromatic multifunctional epoxy resins are:

Polyglycidyl and poly(β -methylglycidyl) ethers which may be obtained by reacting a compound containing at least two phenolic hydroxyl groups in the molecule with epichlorohydrin, glycerol dichlorohydrin or with β -methyl epichlorohydrin under alkaline conditions or in the presence of an acid catalyst, and subsequent treatment with an alkali. Illustrative of compounds containing at least two phenolic hydroxyl groups in the molecule are alcohols containing aromatic groups such as N,N-bis-(2-hydroxyethyl)aniline or p,p'-bis-(2-hydroxyethylamino)diphenylmethane, or mono- or polynuclear polyphenols such as resorcinol, hydroquinone, bis(4-hydroxyphenyl)methane, 2,2-bis-(4-hydroxyphenyl)propane, brominated 2,2-bis-(4-hydroxyphenyl)propane, bis-(4-hydroxyphenyl) ether, bis-(4-hydroxyphenyl)sulfone, 1,1,2,2-tetrakis(4-hydroxyphenyl) ethane or novolaks which are obtainable by condensation of aldehydes such as formaldehyde, acetaldehyde, chloral or furfuraldehyde with phenols or alkyl- or halogen-substituted phenols such as phenol, the above described bisphenols, 2- or 4-methylphenol, 4-tert-butylphenol, p-nonylphenol or 4-chlorophenol.

Poly(N-glycidyl) compounds which may be obtained by dehydrochlorinating the reaction products of epichlorohydrin with amines which contain at least two amino hydrogen atoms. Amines from which these epoxy resins are derived are, typically, aromatic amines such as aniline, p-toluidine, bis-(4-aminophenyl) methane, bis-(4-aminophenyl) ether, bis-4-(4-aminophenyl)sulfone, 4,4'-diaminobiphenyl or 3,3'-diaminobiphenyl, or aliphatic amines such as m-xylylenediamine.

Poly(S-glycidyl) derivatives, for example bis(S-glycidyl) derivatives which are derived from bis-(4-mercaptomethylphenyl) ether.

It is also possible, however, to use epoxy resins in which the 1,2-epoxy groups are attached to different hetero atoms or functional groups. These compounds comprise, for example, the N,N,O-triglycidyl derivative of 4-aminophenol, the N,N,O-triglycidyl derivative of 3-aminophenol or the glycidyl ether/glycidyl ester of salicylic acid.

Preferred aromatic multifunctional epoxy (meth)acrylates include acrylated diglycidyl ether bisphenol A, acrylated epoxy novolacs, amino modified bisphenol A epoxy acrylates, rubber modified acrylated epoxies and fatty acid modified epoxy acrylates.

The aromatic multifunctional epoxy (meth)acrylate is present in a range of from about 10 to about 60% by weight, preferably about 10 to about 40% by weight, most preferably about 20 to about 30% by weight.

At least one free radical polymerizable monomer is included as a diluent. Suitable free radical polymerizable monomers include vinylic coreactants such as N-vinyl pyrrolidone, N-vinyl caprolactam and N,N-dimethylacrylamide, alkyl ne glycol vinyl ethers, vinyl toluene, styrene, divinyl benzene and thiol, acrylates and methacrylates such as ethylene glycol dimethacrylate, isobornyl acrylate, phenoxyethyl acrylate, acrylates and methacrylates of polyols such as trimethylol propane trimethacrylate and pentaerythritol triacrylate, allylic com-

pounds such as triallyl isocyanurate, diallylphthalate, tetraallyl pyromellitate, o,o'-diallyl bisphenol A, eugenol, aryl allyl ethers such as the diallyl ether of bisphenol A, acrylic ester with 3-(2-hydroxyethyl)-2-oxazolidone, 2-propenoic acid-2-[[1-methyl ethoxy carbonyl]amino] ethyl ester and the like. N-vinyl pyrrolidone, N-vinyl caprolactam, acrylic ester with 3-(2-hydroxyethyl)-2-oxazolidone, 2-propenoic acid-2-[[1-methyl ethoxy carbonyl]amino] ethyl ester, N,N-dimethylacrylamide and phenoxyethyl acrylate are preferred.

The free radical polymerizable monomer is present in an amount of from about 5 to about 40% by weight, preferably about 10 to about 30% by weight, most preferably about 20 to about 30% by weight.

Illustrative of suitable free radical photoinitiators for use in the composition according to the present invention are 2,2-diethoxyacetophenone, 2- or 3- or 4-bromoacetophenone, 3- or 4-allylacetophenone, 2-acet-
 10 onaphthone, benzaldehyde, benzoin, the alkyl benzoin ethers, benzophenone, benzoquinone, 1-chloroanthraquinone, p-diacetyl-benzene, 9,10-dibromoanthracene, 9,10-dichloroanthracene, 4,4-dichlorobenzophenone, thioxanthone, 2-chlorothioxanthone, methylthioxanthone, α,α,α -trichloro-para-t-butyl acetophenone, 4-methoxybenzophenone, 3-chloro-8-nonyloxanthone, 3-iodo-7-methoxyxanthone, benzaldehyde, carbazole, 4-chloro-4'-benzyl-benzophenone, fluorene, fluorenone, 1,4-naphthylphenylketone, 2,3-pentanedione, 2,2-di-
 15 sec-butoxy acetophenone, dimethoxyphenyl acetophenone, propiophenone, chlorothioxanthone, xanthone and the like, or mixtures of these. The foregoing list is meant to be illustrative only and is not meant to exclude any suitable photoinitiators known to those skilled in the art. Preferably, the photoinitiator used is dimethoxyphenyl acetophenone. The photoinitiator is present in an amount of from about 0.1 to about 5.0 % by weight, preferably about 0.1 to about 3.0 % by weight, most preferably about 1 to about 3 % by weight.

Those skilled in the art of photochemistry are fully aware that photoactivators can be used in combination with the aforementioned photoinitiators and that synergistic effects are sometimes achieved when such combinations are used. Photoactivators are well known in the art and require no further description to make known what they are and the concentrations at which they are effective. Nonetheless, one can mention as illustrative of suitable photoactivators, methylamine, tributylamine, methyldiethanolamine, 2-aminoethylethanolamine, allylamine, cyclohexylamine, cyclopentadienylamine, diphenylamine, ditolylamine, triethylamine, tribenzylamine, n-cyclohexyl-ethylenimine, piperidine, N-methylpiperazine, 2,2-dimethyl-1,3-bis(3-N-morpholinyl) propionyloxypropane, and the like, or any combination of these.

The compositions of this invention can also be cured upon exposure to any source of radiation emitting actinic radiation at a wavelength within the ultraviolet spectral region. Suitable sources of radiation include mercury, xenone, carbon arc lamps, etc. Exposures may be from less than about 1 second to 10 minutes or more depending upon the amounts of particular polymerizable materials and photoinitiator being utilized and depending upon the radiation source and distance from the source and the thickness of the coating to be cured. The compositions may also be photopolymerized by exposure to electron beam radiation. Generally speaking the dosage necessary is from less than 1 megarad to 100 megarads or more.

The compositions of the invention may also contain other conventional modifiers such as extenders, fillers and reinforcing agents, pigments, dyestuffs, organic solvents, plasticizers, tackifiers, rubbers, diluents, and the like. As extenders, reinforcing agents, fillers and pigments which can be employed in the compositions according to the invention there may be mentioned, for example, glass fibers, glass balloons, boron fibers, carbon fibers, cellulose, polyethylene powder, polypropylene powder, mica, asbestos, quartz powder, gypsum, antimony trioxide, bentonites, talc, silica aerogel ("Aerosil"), fumed silica, lithopone, barite, calcium carbonate, titanium dioxide, carbon black, graphite, iron oxide, or metal powders such as aluminum powder or iron powder. The preferred fillers are glass balloons and sodium potassium aluminum silicate. It is also possible to add other usual additives, for example, agents for conferring thixotropy, flow control agents such as silicones, cellulose acetate butyrate, polyvinyl butyral, stearates and the like.

A vertical type high-speed agitator, kneading machine, roll machine, ball mill or any other suitable mixing and agitating machine may be used for dispersion of the components of the composition of the present invention.

The radiation curable composition of this invention exhibits at 25°C (i) a Tg greater than about 45°C, (ii) an elongation of greater than about 3%, (iii) a tensile strength of greater than about 9 N/mm² and (iv) a shear storage modulus (G') of greater than about 30 N/mm². Preferred compositions are those which exhibit at 25°C (i) a Tg between about 50°C and about 120°C, (ii) an elongation between about 3% and about 8%, (iii) a tensile strength between about 13.8 N/mm² and about 20.7 N/mm² and (iv) a shear storage modulus (G') between about 30 N/mm² and about 300 N/mm².

The radiation curable composition of this invention is particularly suitable in adhesive applications requiring a combination of chemical, temperature and fatigue resistance, in particular in the construction of oil and chemical filters, ducts, their flexibility, impact resistance, hardness, thermal resistance, chemical resistance, fatigue resistance and adhesion to rigid, resilient and flexible substrates, such as metal, plastic, glass, rubber, paper, wood and ceramics.

The following examples serve to give specific illustration of the practice of this invention but they are not intended in any way to act to limit the scope of this invention.

Example 1:

This example illustrates the preparation of a typical mixture of acrylates urethanes (Component 1) with the addition of N-vinyl pyrrolidone:

<u>Reactants</u>	<u>% by weight</u>
PLURACOL [®] P220 (polyether polyol from BASF, Parsippany, N.J.)	56.11
MONDUR [®] M Flaked MDI (1,1-methylene-bis-4-isocyanatobenzene from Mobay, Pittsburg PA)	17.455
TONE [®] 0310 polycaprolactone triol (Union Carbide Corporation)	2.65
BHT Intermediate (mixture of hydroxyethylmethacrylate and butylated hydroxyl toluene in a 99.601 to 0.309 ratio)	14.695
N-vinyl pyrrolidone	9.09

The reaction vessel is cleaned, dried and deaired by drawing a vacuum and releasing the vacuum with nitrogen. The temperature is set to 71 °C. With a nitrogen purge, the 1,1-methylene-bis-(4-isocyanatobenzene) is charged to the reaction vessel. After all the 1,1-methylene-bis-(4-isocyanatobenzene) has been added to the reaction vessel, a non-metallic paddle is used to evenly distribute the flakes at the bottom of the reaction vessel to melt. After the 1,1-methylene-bis-(4-isocyanatobenzene) is liquid, the polyether polyol is quickly added to the reaction flask with the agitator set on high. The polycaprolactone triol is then added. The reaction is allowed to exotherm to 82°C or the reaction is heated and maintained between 79-85°C. The reaction is continued until the NCO content is less than 6.60%. The nitrogen blanket is then removed, the temperature is maintained between 79-82°C and the BHT intermediate is added in three equal portions at 45 minute intervals. The reaction is continued until the NCO content is less than 0.30%. N-vinyl pyrrolidone is then added to the reaction mixture, the agitator is reduced to low and the reaction mixture stirred for 30 minutes. The reaction mixture is then cooled to between 63-68°C.

Example 2:

This example illustrates the preparation of another typical mixture of acrylated urethanes (Component 1) using the procedure set forth in Example 1:

<u>Reactants</u>	<u>% by weight</u>
PLURACOL [®] P220 (polyether polyol from BASF, Parsippany, N.J.)	61.5
MONDUR [®] M Flaked MDI (1,1-methylene-bis-4-isocyanatobenzene from Mobay, Pittsburg PA)	19
TONE [®] 0310 polycaprolactone triol (Union Carbide Corporation)	3
BHT Intermediate (mixture of hydroxyethylmethacrylate and butylated hydroxyl toluene in a 99.601 to 0.309 ratio)	16.5

Examples 3-7:

These examples illustrate the preparation of typical compositions of the present invention. The formulations are provided in Table 1 and the chemical and physical properties of the cured products are provided in Tables 2 (all percentages are on a weight basis unless indicated otherwise):

Table 1

<u>Reactants*</u>	<u>Examples</u>				
	3	4	5	6	7
Example 1	55.0	44.0	64.9	88.6	59.4
EBECRYL [®] 3700	20.0	30.0	10.0	--	--
NVP	--	1.0	4.1	2.4	3.0
PEA	13.0	13.0	--	--	--
TMPTA	10.0	10.0	10.0	--	--
IRGACURE [®] 651	2.0	2.0	1.0	2.5	3.0
IBOA	--	--	10.0	4.5	6.7
IDA	--	--	--	2.0	--

* Description of Reactants

Example 1	Component 1 with 9.09% N-vinylpyrrolidone
EBECRYL [®] 3700	Acrylated epoxy from Radcure Specialties, Louisville, Ky
NVP	N-vinylpyrrolidone

PEA	Phenoxyethyl acrylate
TMPTA	Trimethylolpropane triacrylate -Ageflex TMPTA from CPS Chemical
IRGACURE [®] 651	dimethoxyphenyl acetophenone from CIBA-GEIGY Corporation, Ardsley, N.Y.
IBOA	Isobornyl acrylate
IDA	Isodecyl acrylate

The formulations are cured using the following conditions:

Radiation Wavelength:	Fusion Systems D Bulb (Rockville, MD)
Cure Time:	90 seconds
Distance Source from Specimen:	53 mm (Focus of the reflector)
Total Cure Dose:	4.32 W/cm ²
Shore D Hardness:	65-75
Refractive Index (25°C Uncured):	1.505-1.515
Gardner Color:	< 1

Table 2

<u>Physical Property</u>	<u>Example</u>				
	3	4	5	6	7
T _g * [°C]	111	119	136	120	94
Elongation * [%]	8	3	7	46	36
Tensile Strength * [N/mm ²]	14.4	18.6	8.9	11.3	15.2
Young's Modulus [N/mm ²]	503	979	338	83	221
Shear Storage Modulus (at 25°C [N/mm ²])	262	296	241	76	138
Shear Storage Modulus (at 150°C [N/mm ²])	14	14	21	0.7	7
Shear Loss Modulus (at 25°C [N/mm ²])	21	28	21	7	14
tan δ (25°C)	0.0744	0.0861	0.0832	0.0111	0.0112

* The T_g is determined by rheology using a Rheometrics RDA 700. The percent elongation and tensile strength are measured using ASTM procedure D638-86.

Claims

1. A radiation curable composition with high temperature oil resistance comprising
 - (1) a (meth)acrylated urethane component comprising
 - (a) the reaction product of hydroxyethyl(meth)acrylate and a monomeric or polymeric aromatic iso-

cyanate and

(b) hydroxyethyl(meth)acrylate,

(2) an aromatic multifunctional epoxy (meth)acrylate having a molecular weight of less than about 1000,

(3) at least one free radical polymerizable monomer and

(4) a free radical photoinitiator,

which composition exhibits at 25°C (i) a T_g greater than about 45°C, (ii) an elongation of greater than about 3%, (iii) a tensile strength of greater than about 9 N/mm² and (iv) a shear storage modulus of greater than about 30 N/mm².

2. A radiation curable composition according to claim 1 wherein component (a) is present in an amount ranging from about 50 to about 99% by weight, preferably from about 80 to about 99% by weight, most preferably in an amount of about 94% by weight, based upon the total weight of component (1), and component (b) is present in an amount ranging from about 1 to about 50% by weight, preferably from about 1 to about 20% by weight, most preferably in an amount of 6% by weight, based upon the total weight of component (1).
3. A radiation curable composition according to claim 1 wherein said aromatic isocyanate is selected from the group consisting of methylene bis-(4-isocyanato benzene), toluene diisocyanate, 3,3'-toluidine-4,4'-diisocyanate, 3,3'-dimethyl-diphenylmethane-4,4'-diisocyanate, 1,5-diisocyanato-naphthalene, 1,4-diisocyanato-benzene and 1,4- and 1,3-di-(isocyanato-dimethyl)-benzene.
4. A radiation curable composition according to claim 1 wherein said aromatic isocyanate is monomeric methylene bis-(4-isocyanato benzene).
5. A radiation curable composition according to claim 1 wherein component (a) is the reaction product of hydroxyethylmethacrylate and methylene bis-(4-isocyanato benzene) and is present in an amount of 94% by weight, based upon the total weight of component (1), and component (b) is hydroxyethylmethacrylate and is present in an amount of 6% by weight, based upon the total weight of component (1).
6. A radiation curable composition according to claim 1 wherein component (1) further comprises (c) a (meth)acrylated prepolymer of a monomeric or polymeric aromatic isocyanate and at least one polycaprolactone polyol with a functionality ≥ 2 and a molecular weight in the range of about 500 to about 3000.
7. A radiation curable composition according to claim 6 wherein component (a) is present in an amount ranging from about 5 to about 35% by weight, preferably from about 10 to about 30% by weight, most preferably in an amount of about 23% by weight, based upon the total weight of component (1), component (b) is present in an amount ranging from about 1 to about 20% by weight, preferably from about 1 to about 10% by weight, most preferably in an amount of about 6% by weight, based upon the total weight of component (1), and component (c) is present in an amount ranging from about 50 to about 90 % by weight, preferably from about 70 to about 80% by weight, most preferably in an amount of about 71 % by weight, based upon the total weight of component (1).
8. A radiation curable composition according to claim 6 wherein component (a) is the reaction product of hydroxyethylmethacrylate and methylene bis-(4-isocyanato benzene) and is present in an amount of 23% by weight, based upon the total weight of component (1), component (b) is hydroxyethylmethacrylate and is present in an amount of 6 % by weight, based upon the total weight of component (1), and component (c) is the reaction product of methylene bis-(4-isocyanatobenzene) and a polycaprolactone triol and is present in an amount of about 71 % by weight, based upon the total weight of component (1).
9. A radiation curable composition according to claim 1 wherein component (1) further comprises (d) a (meth)acrylated prepolymer of a monomeric or polymeric aromatic isocyanate and at least one polyether polyol with a functionality ≥ 2 and a molecular weight in the range of about 90 to about 7000.
10. A radiation curable composition according to claim 9 wherein component (a) is present in an amount ranging from about 10 to about 30% by weight, preferably from about 20 to about 30% by weight, most preferably in an amount of about 23% by weight, based upon the total weight of component (1), component (b) is present in an amount ranging from about 1 to about 20% by weight, preferably from about 5 to about 15% by weight, most preferably in an amount of about 6% by weight, based upon the total weight of component (1).

pon nt (1), and component (d) is present in an amount ranging from about 50 to about 90% by weight, preferably from about 60 to about 90% by weight, most preferably in an amount of about 71 % by weight, based upon the total weight of component (1).

- 5 11. A radiation curable composition according to claim 9 wherein component (a) is the reaction product of hydroxyethylmethacrylate and methylene bis-(4-isocyanato benzene) and is present in an amount of about 23% by weight, based upon the total weight of component (1), component (b) is hydroxyethylmethacrylate and is present in an amount of about 6% by weight, based upon the total weight of component (1), and component (d) is the reaction product of methylene bis-(4-isocyanatobenzene) and an a
10 poly(oxypropylene)-poly(oxyethylene) block copolymer and is present in an amount of about 71 % by weight, based upon the total weight of component (1).
12. A radiation curable composition according to claim 1 wherein component (1) further comprises (c) a
15 (meth)acrylated prepolymer of a monomeric or polymeric aromatic isocyanate and at least one polycaprolactone polyol with a functionality ≥ 2 and a molecular weight in the range of about 500 to about 3000 and (d) a (meth)acrylated prepolymer of a monomeric or polymeric aromatic isocyanate and at least one polyether polyol with a functionality ≥ 2 and a molecular weight in the range of about 90 to about 7000.
- 20 13. A radiation curable composition according to claim 12 wherein component (a) is present in an amount ranging from about 10 to about 50% by weight, preferably from about 20 to about 30% by weight, most preferably in an amount of about 23% by weight, based upon the total weight of component (1), component (b) is present in an amount ranging from about 1 to about 20% by weight, preferably from about 5 to about 15% by weight, most preferably in an amount of about 6% by weight, based upon the total weight of component (1), component (c) is present in an amount ranging from about 1 to about 10% by weight, preferably from about 1 to about 5 % by weight, most preferably in an amount of about 3% by weight, based upon
25 the total weight of component (1), and component (d) is present in an amount ranging from about 25 to about 75% by weight, preferably from about 50 to about 75% by weight, most preferably in an amount of about 68% by weight, based upon the total weight of component (1).
- 30 14. A radiation curable composition according to claim 12 wherein component (a) is the reaction product of hydroxyethylmethacrylate and methylene bis-(4-isocyanato benzene) and is present in an amount of about 23% by weight, based upon the total weight of component (1), component (b) is hydroxyethylmethacrylate and is present in an amount of about 6% by weight, based upon the total weight of component (1), component (c) is the reaction product of methylene bis(4-isocyanatobenzene) and a polycaprolacton
35 triol and is present in an amount of about 3% by weight, based upon the total weight of component (1), and component (d) is the reaction product of methylene bis-(4-isocyanatobenzene) and an a poly(oxypropylene)-poly(oxyethylene) block copolymer and is present in an amount of about 68% by weight, based upon the total weight of component (1).
- 40 15. A radiation curable composition according to claim 1 wherein said aromatic multifunctional epoxy (meth)acrylate is selected from the group consisting of acrylated diglycidyl ether bisphenol A, acrylated epoxy novolacs, amino modified bisphenol A epoxy acrylates, rubber modified acrylated epoxies and fatty acid modified epoxy acrylates.
- 45 16. A radiation curable composition according to claim 1 wherein said aromatic multifunctional epoxy (meth)acrylate is present in an amount from about 10 to about 60% by weight, preferably from about 10 to about 40% by weight and most preferably from about 20 to about 30% by weight.
- 50 17. A radiation curable composition according to claim 1 wherein said free radical polymerizable monomer is selected from the group consisting of N-vinyl pyrrolidone, N-vinyl caprolactam, acrylic ester with 3-(2-hydroxyethyl)-2-oxazolidone, 2-propenoic acid-2[[1-methyl ethoxy carbonyl]amino] ethyl ester, N,N-dimethylacrylamide and phenoxyethyl acrylate.
- 55 18. A radiation curable composition according to claim 1 wherein said free radical polymerizable monomer is present in an amount of from about 5 to about 40% by weight, preferably from about 10 to about 30% by weight and most preferably from about 20 to about 30% by weight.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 92810620.2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	<u>US - A - 4 690 987</u> (SAKAKIBARA et al.) * Claim 1; comparative example 1; comparative applications example 1; column 1, lines 36-54; column 2, lines 53-68; column 4, lines 30-44 * --	1-3, 15	C 08 L 75/16 C 08 L 63/10
A	<u>DE - A - 3 426 043</u> (KULZER & CO GMBH) * Examples 1.1, 1.2, 2; claims 1, 2, 4, 5, 8-11 * --	1, 2, 15	
A	<u>US - A - 4 260 703</u> (HODAKOWSKI et al.) * Claims 1, 6, 8, 9 * --	1-3, 9	
A	<u>DE - A - 3 045 788</u> (BAYER AG) * Comparative example 12; examples 2, 5; application examples A, C; claims 1, 2 * ----	1	TECHNICAL FIELDS SEARCHED (Int. CL.5) C 08 L 75/00 C 08 L 63/00 C 08 L 101/00 C 08 G 18/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 16-11-1992	Examiner SEIRAFI
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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